

Effect of transition metals addition on the catalyst of manganese/titania for low-temperature selective catalytic reduction of nitric oxide with ammonia

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Received 15 October 2006; received in revised form 26 September 2007; accepted 29 September 2007

Available online 5 October 2007

Abstract

To retard the sintering, a series of transition metals were added to the low-temperature SCR catalysts based on Mn/TiO₂, and activity of these catalysts was investigated. It was found that the transition metal had significant effects on the catalytic activity. With the addition of transition metals, more NO could be removed at lower temperature. The temperature of 90% NO conversion could decrease to 361 K by using Fe(0.1)–Mn(0.4)/TiO₂. The results of X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction spectra (EDS) indicated that manganese oxides and titania could be better dispersed in the catalyst, and higher catalytic activity was obtained. From X-ray photoelectron spectrum (XPS) it could be known that solid solution was formed among the transition metal, manganese oxides and titania. With the formation of this solid solution, the Brunauer–Emmett–Teller (BET) area and pore volume increased. Furthermore, the in situ diffuse reflectance infrared transform spectroscopy (DRIFT) results showed that by using these catalysts, more NO could be oxidized to NO₂ and nitrate, and then reacted with NH₃. Therefore, the catalytic activity was greatly improved by the addition of transition metals.

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Keywords: Sol–gel method; NO removal; Low-temperature SCR; Transition metal; Solid solution

1. Introduction

In recent years, there is a rising interest in developing a low-temperature (353–523 K) SCR catalyst for the removal of NO_x. Since by using this kind of catalyst, the deNO_x reactor can be moved to downstream of the desulphurization scrubber and/or particulate control device, where most of sulphur dioxide and dust is removed and then its deactivation effect can be weakened.

Manganese oxides attract interest due to its high SCR activity at low temperature [1,2]. The manganese oxides contain various types of labile oxygen, which are necessary to complete a catalytic cycle [3,4]. Among the different types of manganese oxide catalysts, it was reported [5,6] that the amorphous manganese oxide had good performance in SCR

reaction, while the crystalline one contributed little to activity. And it was known from previous studies [7,8] that the dispersion of manganese oxide played an important role in the formation of amorphous phase.

However, during the process of catalyst preparation, the sintering always exists, leading to a bad dispersion of active component [9]. Recently, there were some investigations on the bimetallic and ternary mixed-oxides catalysts. In their work, it was suggested that the sintering could be reduced in these catalysts, which had a better thermal stability and a longer lifetime than the monometallic catalyst [10]. As for Pt/Fe/γ-Al₂O₃ catalyst [11], the Pt particles were covered with ferric oxides, which prevented the catalyst from sintering at high calcining temperature in an oxidizing atmosphere. For low-temperature SCR, it was presented [5] that when Fe was induced in the catalysts, the efficiency of NO removal increased. Furthermore, some other metals were also added to the catalysts to enhance the catalytic activity [12–14]. Therefore, the ternary mixed-oxides catalyst may be a prospective catalyst in low-temperature SCR system. The purpose of this study is to clarify the effect of transition metals

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addition on the activity of Mn/TiO₂ for low-temperature SCR of NO.

In this paper, the catalysts based on Mn/TiO₂ with the addition of transition metals were studied to remove NO with NH₃ at low temperature. The catalysts were prepared by sol–gel method, and transition metals (including Fe, Cu, Ni and Cr) were selected added to Mn/TiO₂.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by sol–gel method. All chemicals used were of analytical grade. Butyl titanate (0.1–0.3 mol), ethanol (0.8 mol), water (0.6 mol), acetic acid (0.3 mol) and manganese nitrate were mixed under vigorous stirring at room temperature, formed a transparent yellow sol. The nitrates of transition metals (Fe, Cu, Ni and Cr) were dissolved in the ethanol (0.3 mol) and water (0.4 mol), and then added dropwisely to the sol. The transparent yellow sol was transformed to red one gradually. This sol was kept at 298 K for 10 days, and it transformed to gel. Simultaneously, the color of this gel became black. The gel was dried at 378 K to remove the organic solution. During this process, the volume of the gel decreased progressively, and the gel transformed to porous solid. Then the solid was crushed and sieved to 60–100 mesh and calcined at 773 K in air for 6 h in a tubular furnace. The catalyst was denoted as M(y)–Mn(z)/TiO₂, where M represents the transition metals, and y and z represent the mole ratio of the transition metal and Mn to Ti, respectively, e.g., Fe(0.1)–Mn(0.4)/TiO₂.

2.2. Catalytic activity measurement

The SCR activity measurement was carried out in a fixed-bed, stainless steel reactor. The reactor (i.d. 1 cm) consisted of a steel tube in which 4 ml of catalyst was placed. The experiments were performed under atmospheric pressure at 353–483 K. The typical composition of the reactant gas was: NO of 1000 ppm, NH₃ of 1000 ppm, O₂ of 3%, and balanced N₂. And the total flow rate was 2000 ml/min. The reaction temperature was controlled by an OMRON programmable temperature controller. The concentration of NO, NO₂, and O₂ was monitored by a flue gas analyzer (KM9106 Quintox Kane International Limited), which was standardized by chemical methods. In order to confirm that the decrease of NO was not caused by the adsorption of NO in the catalysts, at the beginning of each experiment, the catalyst was purged with reactant gas until there was no difference between the inlet and the outlet gas.

2.3. Characterization of the samples

Adsorbed-1 Quantachrom was used to calculate the surface area and pore volume of the samples. X-ray diffraction (XRD) measurements were carried out with a XD-2 X-ray diffractometer using Cu K α radiation. X-ray photoelectron spectrum

(XPS) measurements were used to determine the atomic concentration and the state of the elements on catalyst surface by a V.G. Scientific Escalab 250 with Al K α X-rays ($h\nu = 1486.6$ eV). The concentration of transition metals, Mn, Ti, and O on the surface of the samples was calculated from the integral of peak areas of the XPS data divided by each sensitivity factor of the element using the Avantage data processing system provide by Thermo Electron Corporation. Transmission electron microscopy (TEM) and electron diffraction spectra (EDS) were used to investigate the microstructures of the prepared samples and the dispersion of the elements with a JOEL JEM-2010 electron microscope.

Fourier transform infrared spectroscopy (FTIR) spectra were acquired using in situ diffuse reflectance infrared transform spectroscopy (DRIFT) cell equipped with gas flow system. The DRIFT measurements were performed with Nicolet 5700 FTIR spectrometers at 4 cm^{−1} resolution with 64 co-added scans. In DRIFT cell, the catalyst was pretreated at 773 K in He environment for 2 h, then cooled to 423 K. The background spectrum was recorded in flowing He and was subtracted from the sample spectrum.

3. Results and discussion

3.1. Activity of Mn/TiO₂ catalyst

Fig. 1 showed the NO conversion by using Mn/TiO₂ catalysts with different molar ratios of Mn/Ti at different temperatures. It could be found from Fig. 1 that there was neglected efficiency on the pure TiO₂. After the addition of Mn, the activity increased rapidly. Higher manganese loading would enhance NO conversion until the mole ratio of Mn/Ti reached 0.4. Beyond this value, a further increase of manganese loading would do harm to the activity. It was suggested by the previous study [15] that there was an optimal value of Mn loading. When it was beyond a certain value, sintering would take place in the catalyst, leading to the reduction of NO conversion. In this investigation, by using the catalysts based on Mn/TiO₂, the

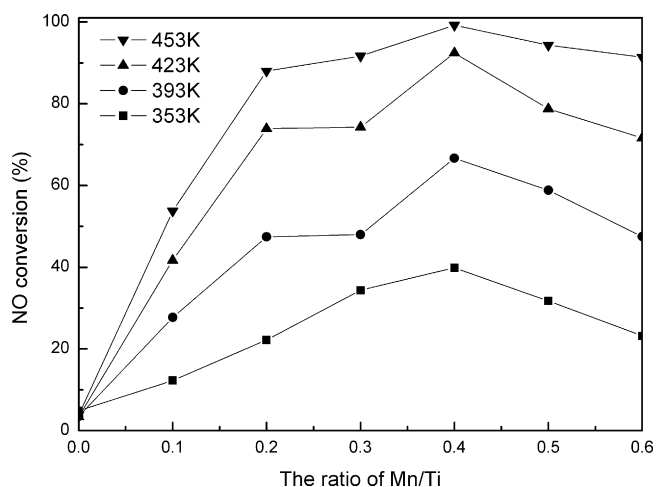


Fig. 1. The variation of NO conversion with Mn/TiO₂ catalysts with different ratio of Mn/Ti at different temperatures. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 3%, balance N₂, total flow rate 2000 ml/min, catalyst 4 ml.

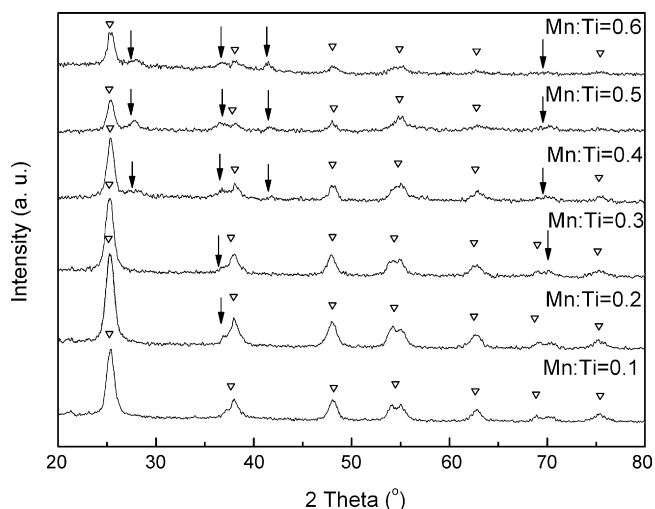


Fig. 2. XRD spectra of manganese supported on titania (▽, anatase; ↓, MnO₂).

optimal value of manganese loading was Mn/Ti = 0.4 (see Fig. 1).

Fig. 2 showed the XRD patterns of the Mn/TiO₂ catalysts with different Mn loading. It had been mentioned in Section 1 that SCR activity was relative to the dispersion of manganese oxides. When manganese oxides could not be well dispersed in the catalyst, the amorphous manganese oxides would transform to crystalline phase, which contributed little to activity [5]. From the X-ray diffraction, it could be seen that at low loadings (Mn/Ti < 0.2), none of the XRD spectra gave intense peaks for manganese oxides due to the high dispersion and/or low crystalline nature of the manganese oxides. When the Mn loading was 0.2, MnO₂ at 2θ values of 37.1 was observed as the only phase for the supported manganese oxide catalysts. With the Mn loading continued increasing, the crystal phase of MnO₂ became apparent. When the ratio of Mn/Ti was more than 0.4, there were apparent peaks due to crystal phase of MnO₂ formed in the catalyst. It indicated that when Mn loading was larger than 0.4, the sintering took place and then led to the formation of the well-ordered crystalline MnO₂, which contributed little to NO removal. Therefore, when the ratio of Mn/Ti increased from 0.4 to 0.6, the reduction of NO conversion was due to the transformation of the amorphous manganese oxides to crystal phase.

3.2. Activity of the catalysts with transition metals

According to the previous study [16], transition metals had positive effect on the activity of catalysts. In this investigation, to retard the sintering in the catalyst, transition metals (including Fe, Cu, Ni and Cr) were added to Mn(0.4)/TiO₂ and Mn(0.6)/TiO₂. In Fig. 3, it could be seen that in low-temperature window (340–483 K), the catalytic activity was greatly improved by the addition of transition metals. And as shown in Fig. 4, by using the catalysts with transition metals, the temperature of 90% NO conversion decreased greatly. Furthermore, when the ratio of Mn/Ti increased to 0.6, the negative effect of increasing Mn loading was weakened.

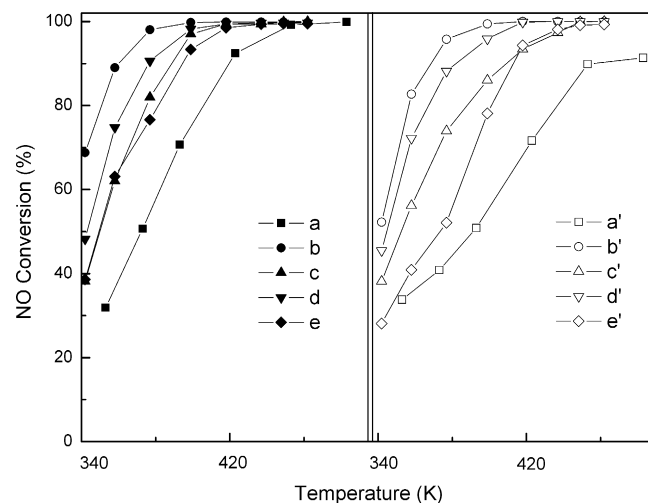


Fig. 3. The variation of NO conversion at different temperatures: (a) Mn(0.4)/TiO₂; (a') Mn(0.6)/TiO₂; (b) Fe(0.1)–Mn(0.4)/TiO₂; (b') Fe(0.1)–Mn(0.6)/TiO₂; (c) Cu(0.1)–Mn(0.4)/TiO₂; (c') Cu(0.1)–Mn(0.6)/TiO₂; (d) Ni(0.1)–Mn(0.4)/TiO₂; (d') Ni(0.1)–Mn(0.6)/TiO₂; (e) Cr(0.1)–Mn(0.4)/TiO₂; (e') Cr(0.1)–Mn(0.6)/TiO₂. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 3%, balance N₂, total flow rate 2000 ml/min, catalyst 4 ml.

Among the metals, Fe had the most significant effect on the catalytic activity. The temperature of 90% NO conversion was about 420 K for Mn(0.4)/TiO₂, and it increased to 451 K when the ratio of Mn/Ti increased to 0.6. After Fe was added, at about 361 K, more than 90% of NO had been converted. And when the ratio of Mn/Ti increased from 0.4 to 0.6, the temperature of 90% NO conversion only increased about 8 K. According to the conclusion of Section 3.1, catalytic activity was related to crystallization of manganese oxides. Thus, it was possible to assume that the transition metals could reduce the crystallinity of the manganese oxides and weaken the sintering in the catalysts. To investigate the effects of transition metals on the catalyst, in Section 3.3, the catalysts would be characterized and analyzed.

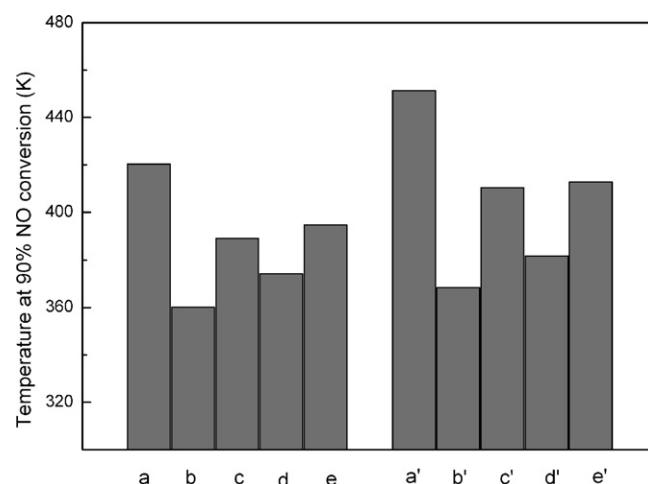


Fig. 4. The variation of temperature at 90% NO conversion: (a) Mn(0.4)/TiO₂; (a') Mn(0.6)/TiO₂; (b) Fe(0.1)–Mn(0.4)/TiO₂; (b') Fe(0.1)–Mn(0.6)/TiO₂; (c) Cu(0.1)–Mn(0.4)/TiO₂; (c') Cu(0.1)–Mn(0.6)/TiO₂; (d) Ni(0.1)–Mn(0.4)/TiO₂; (d') Ni(0.1)–Mn(0.6)/TiO₂; (e) Cr(0.1)–Mn(0.4)/TiO₂; (e') Cr(0.1)–Mn(0.6)/TiO₂.

Table 1
The physical characteristics of Mn(0.4)/TiO₂ and M(0.1)–Mn(0.4)/TiO₂

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Mn(0.4)/TiO ₂	75.3	3.7×10^{-2}	5.57
Fe(0.1)–Mn(0.4)/TiO ₂	112.6	5.6×10^{-2}	5.38
Cu(0.1)–Mn(0.4)/TiO ₂	105.0	5.2×10^{-2}	5.21
Ni(0.1)–Mn(0.4)/TiO ₂	116.9	5.8×10^{-2}	5.34
Cr(0.1)–Mn(0.4)/TiO ₂	112.7	5.6×10^{-2}	5.20

3.3. Characterization of the catalysts

The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size of the catalysts were summarized in Table 1. The surface area of Mn(0.4)/TiO₂ was 75.3 m²/g, and the pore volume was 3.7×10^{-2} cm³/g. After the transition metals were added, the surface area and the pore volume increased greatly. However, it could be seen that there was little change of the average pore size after transition metals were added. Because the volume of the catalyst would decrease progressively during the preparation (as mentioned in Section 2.1), it could be concluded that in the catalysts with the addition of transition metals, a lot of micropore could be preserved and the surface area was larger than that of Mn(0.4)/TiO₂. Therefore, the addition of transition metals had changed the nano-structure of the catalyst.

The concentration of the atom on the surface of the catalysts was determined by XPS. The results were summarized in Table 2. In the XPS analysis, the concentration of Mn and Ti on the surface of the catalysts with transition metals was much higher than that of Mn(0.4)/TiO₂. These variations led to the increase of the catalytic activity (as shown in Figs. 3 and 4). Thus, transition metals addition would influence the dispersion of manganese oxides in the catalysts.

The XRD spectra of the catalysts were shown in Fig. 5. The XRD profile of Mn(0.4)/TiO₂ showed six diffraction peaks, at $2\theta = 25.2^\circ$, 38.0° , 48.1° , 54.5° , 62.8° and 75.3° , corresponding to TiO₂. And other peaks corresponded to crystal phase of MnO₂. When the transition metals were added, the intensity of all of the peaks corresponded to crystal phase of MnO₂ decreased, indicating the decrease of the crystallinity of manganese oxides.

From Table 2 it could be known that the Mn concentration on the surface of M(0.1)–Mn(0.4)/TiO₂ was higher than Mn(0.4)/TiO₂. And the results of Fig. 5 indicated that the enrichment of

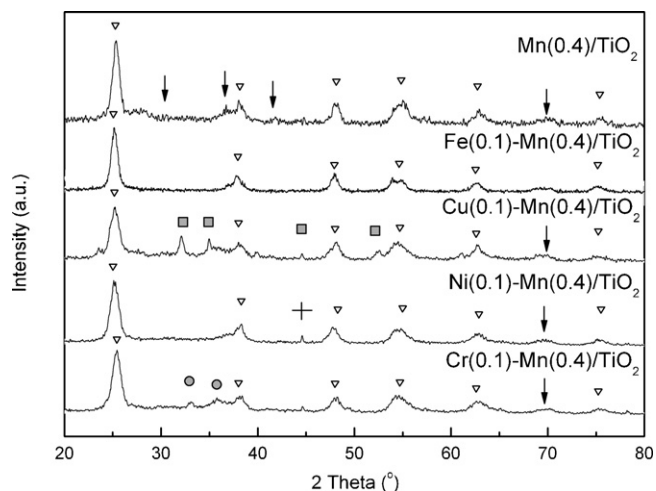


Fig. 5. XRD spectra of Mn(0.4)/TiO₂ and M(0.1)–Mn(0.4)/TiO₂ (▽, anatase; ↓, MnO₂; □, CuO; ○, CrO₂; +, NiO).

Mn at the surface of the catalyst did not lead to the crystallization and sintering in the catalyst. It implied that the addition of transition metals significantly improved the Mn dispersion in the catalyst and manganese oxides were kept as amorphous phase. Moreover, with the addition of transition metals, all of the diffraction peaks for TiO₂ of the catalysts were a little bit wider and higher in diffraction angle than that of Mn(0.4)/TiO₂, while the intensity of these peaks was lower. Thus, TiO₂ was also influenced by the addition of transition metals. It could be concluded that transition metals had significant effects on the crystallization of manganese oxides and TiO₂. Among the peaks due to transition metal oxides, there were some peaks corresponded to CuO, CrO₂ and NiO. However, there were no intense peaks for ferric oxides. In Figs. 3 and 4, the activity of Fe(0.1)–Mn(0.4)/TiO₂ was higher than other samples. It implied that when the transition metals could be well dispersed in the catalysts, it would exist as amorphous material or incorporated into the manganese oxides or titania phase [17], improving the dispersion of manganese oxides and titania. Therefore, with better dispersion and lower degree of the crystallinity of Mn and Ti, the activity of M(0.1)–Mn(0.4)/TiO₂ could be much better than that of Mn(0.4)/TiO₂, and the negative effect of high Mn loading (>0.4) would be reduced (as shown in Figs. 3 and 4).

Fig. 6(a)–(e) showed the transmission electron microscopy (TEM) micrograph of the catalysts. In the micrograph of Mn(0.4)/TiO₂, the particles were not dispersed well and the diameter of these particles was not uniform. Accurate statistical measurement could not be performed. It was because that the sample had partly agglomerated because of the crystallization. In the micrographs of M(0.1)–Mn(0.4)/TiO₂ catalysts, the particles were better dispersed and the particle size could be determined to be about 10 nm. The surface of these particles was not as smooth as that of Mn(0.4)/TiO₂, and the crystal plane was illegible in the centre of the particles (as the arrow shown), indicating the lower degree of crystallinity of the catalysts, especially in the centre of the particles. Furthermore, EDS was used to investigate the dispersion of Mn in the catalysts. It could

Table 2
Atomic concentrations on the surface of Mn(0.4)/TiO₂ and M(0.1)–Mn(0.4)/TiO₂ obtained with XPS

Catalyst	Metal content (at.%)			
	M	Mn	Ti	O
Mn(0.4)/TiO ₂	0	19.4	20.61	59.99
Fe(0.1)–Mn(0.4)/TiO ₂	2.43	28.86	25.61	43.1
Cu(0.1)–Mn(0.4)/TiO ₂	4.38	22.61	29.07	43.94
Ni(0.1)–Mn(0.4)/TiO ₂	–	24.71	29.16	46.13
Cr(0.1)–Mn(0.4)/TiO ₂	5.03	22.47	27.74	44.76

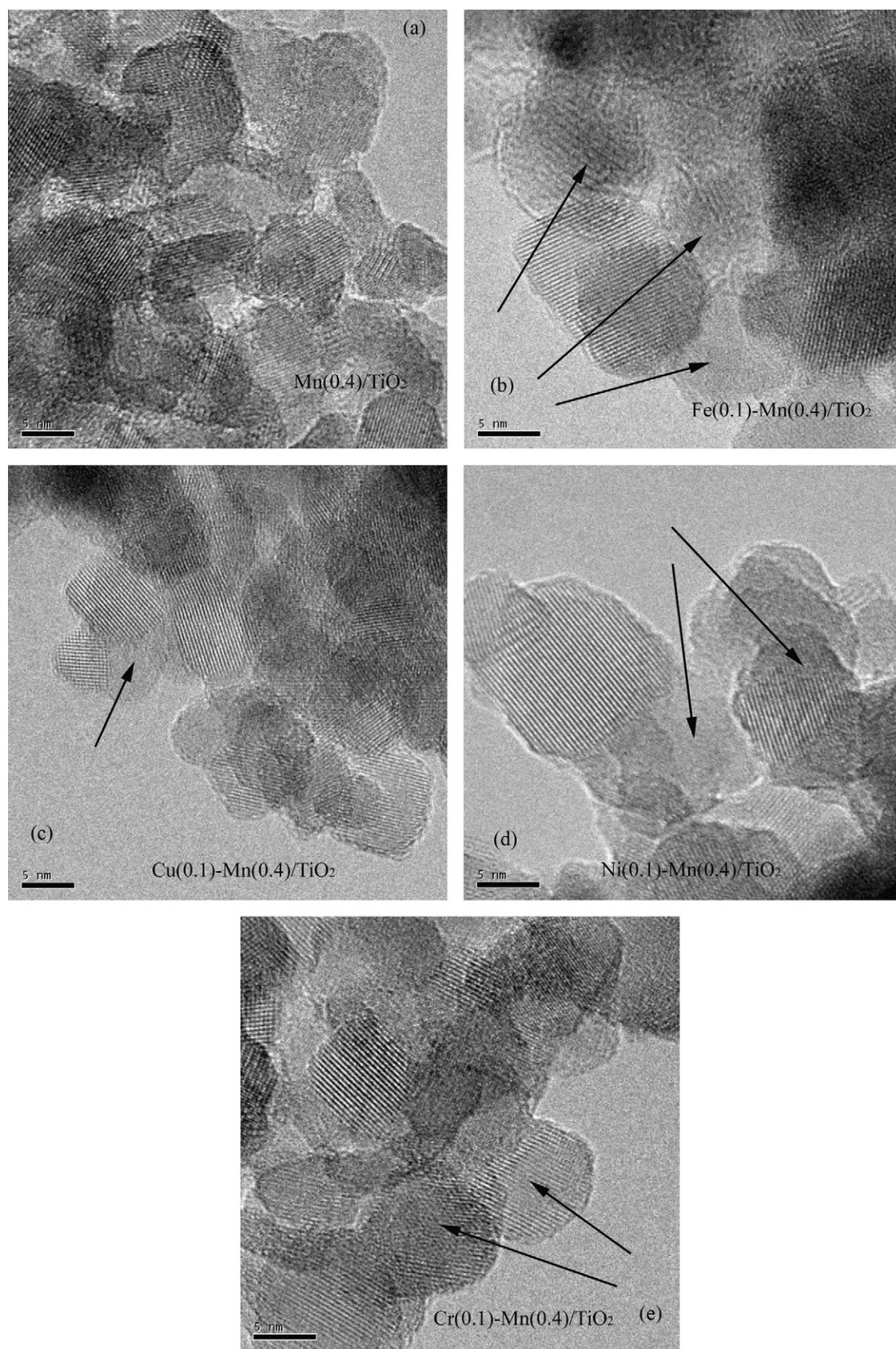


Fig. 6. TEM micrographs of the catalysts.

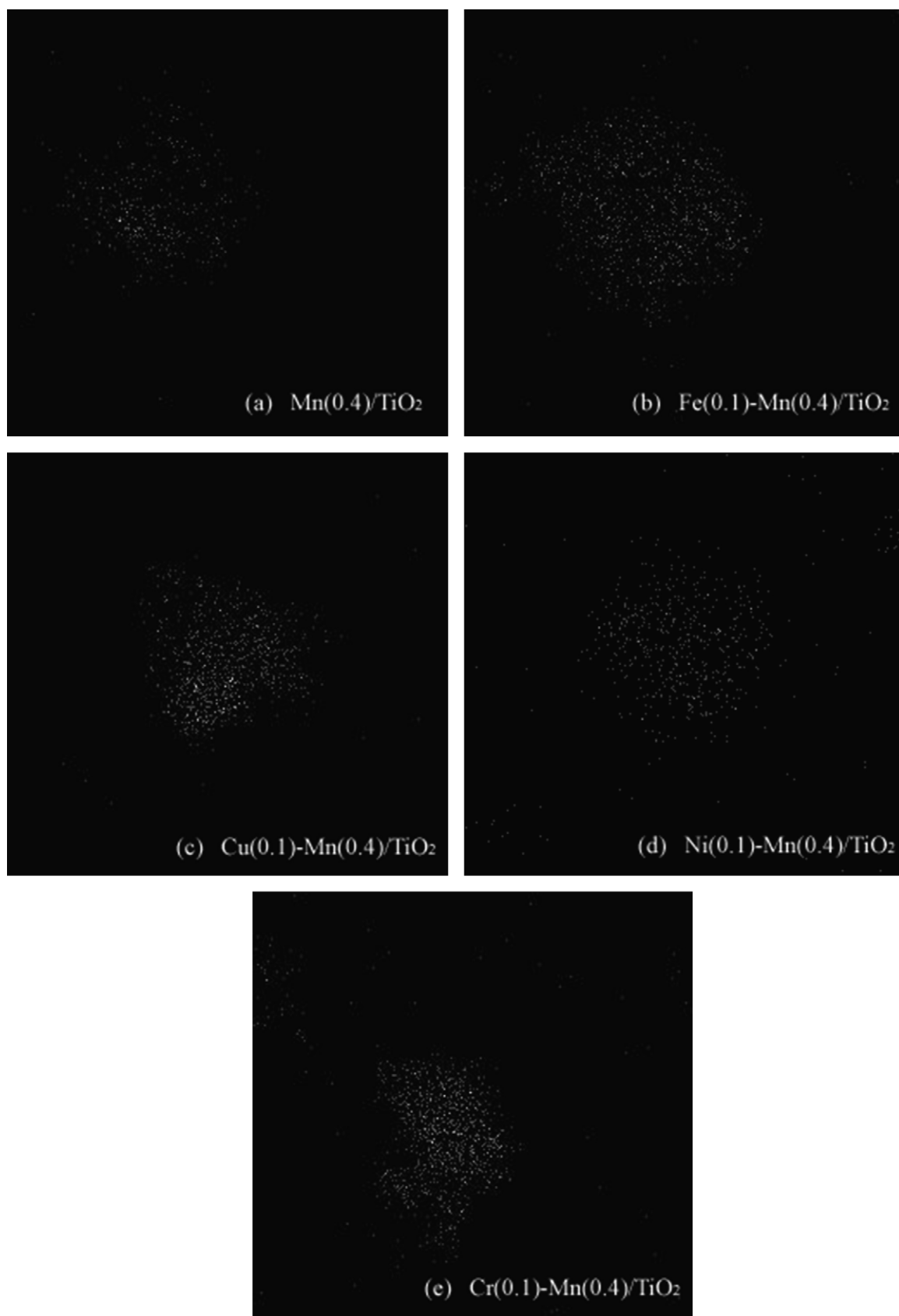


Fig. 7. The dispersion of Mn in the catalysts measured by EDS.

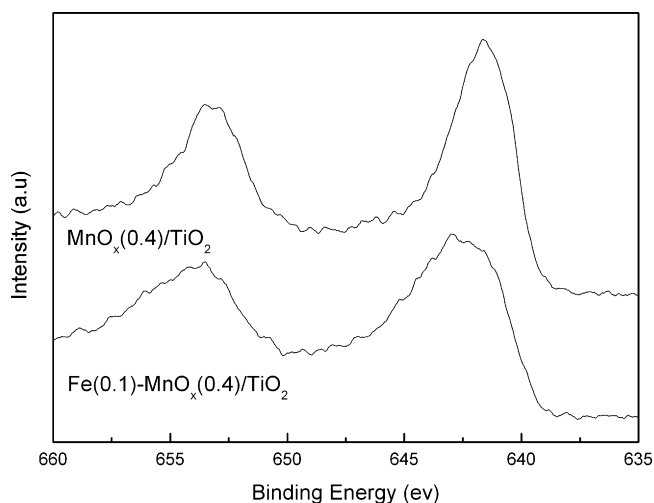


Fig. 8. Mn 2p XPS spectra for Mn(0.4)/TiO₂ and Fe(0.1)-Mn(0.4)/TiO₂.

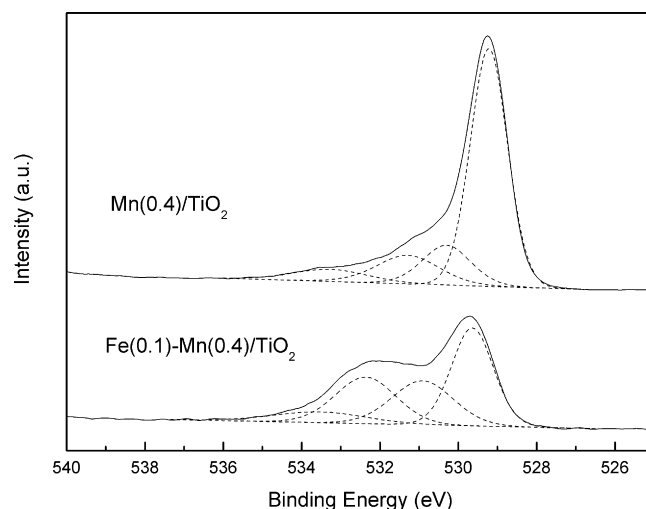


Fig. 10. O 1s XPS spectra for Mn(0.4)/TiO₂ and Fe(0.1)-Mn(0.4)/TiO₂.

be seen in Fig. 7 that the manganese oxides could be dispersed well in the samples.

From the characterization above, it could be known that the concentration of Mn and Ti on the surface of the catalysts increased with the addition of transition metals. And the results of XRD, TEM and EDS showed that the degree of the crystallinity of these catalysts decreased, and the dispersion of the elements was improved. Therefore, there was interaction among the transition metals, Mn and Ti. In the paragraphs below, this interaction was investigated by using XPS and in situ DRIFT, and the influence of the transition metals on the catalysts was studied. Since Fe had the most significant effect on Mn(0.4)/TiO₂, Fe(0.1)-Mn(0.4)/TiO₂ was selected to be investigated.

Mn 2p, Ti 2p and O 1s XPS spectra for the two catalysts were presented in Figs. 8–10, respectively. In Mn 2p spectra, the energy position of the 2p_{3/2} peak was 642.2 eV for Mn(0.4)/TiO₂, indicating that Mn was present in MnO₂ form [18,19]. It was in good agreement with the result of XRD. After Fe was added, the peaks were clearly modified. The peaks of Mn 2p had been broadened and the shapes were more asymmetric. As a general

law, the formation of an interfacial oxide would lead to an energy shift [20] or the presence of satellite peaks [21]. In Fig. 8, the binding-energy value increased from 642.2 to 642.9 eV with the addition of Fe. Furthermore, satellite peaks appeared at 651 and 645 eV, indicating new component was formed [22]. Fig. 9 illustrated Ti 2p XPS spectra for both Mn(0.4)/TiO₂ and Fe(0.1)-Mn(0.4)/TiO₂. For Mn(0.4)/TiO₂, only one oxidation state of titanium was detected, the binding energy for this species being typical for the titanium in oxidation state +4 [23]. However, with the addition of Fe, the intensity of peaks for this oxidation state decreased. Furthermore, in the XPS profile of Fe(0.1)-Mn(0.4)/TiO₂, aside from the contributions from Ti⁴⁺ species, there were several peaks present on the higher binding energy side of the Ti 2p_{1/2} and Ti 2p_{3/2}. Although the exact phase of these peaks were still unknown, it was possible to consider that they were the mixtures of titanium oxides and manganese or ferric oxides. Therefore, it was reasonable to conclude that in the catalyst of Fe(0.1)-Mn(0.4)/TiO₂, part of Mn and Ti had interacted with Fe and formed solid solution on the interface of these metals, and the degree of crystallinity of manganese oxides and titanium oxides greatly decreased. Thus, the dispersion of the elements could be effectively improved, and the active components could be preserved as amorphous phase. Furthermore, in the O 1s spectra (Fig. 10), it could be seen that with the addition of Fe, the intensity of the peak around 529 eV, which due to the lattice oxygen in the metal oxides decreased greatly [1]. It resulted in the decrease of oxygen concentration on the surface of the catalysts (as shown in Table 2).

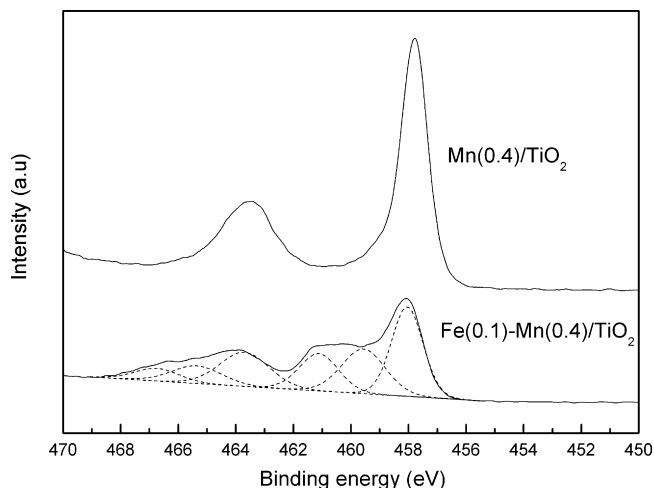


Fig. 9. Ti 2p XPS spectra for Mn(0.4)/TiO₂ and Fe(0.1)-Mn(0.4)/TiO₂.

In situ DRIFT was used to investigate the effect of transition metals on the catalytic process. The spectra covering the range 1000–2000 cm⁻¹ were recorded to elucidate the chemical structure of NO_x species adsorbed on Mn(0.4)/TiO₂ and Fe(0.1)-Mn(0.4)/TiO₂. One thousand parts per million NO and 2% O₂ were introduced to the DRIFT cell for 30 min, and then He was purged for 30 min to remove the gas-phase NO_x. After that the spectra were recorded and shown in Fig. 11. Bands at 1580, 1530, and 1270 cm⁻¹ were detected both on the two catalysts. On Fe(0.1)-Mn(0.4)/TiO₂, the new bands at 1603 and 1250 cm⁻¹ appeared and the bands in the range of 1600–

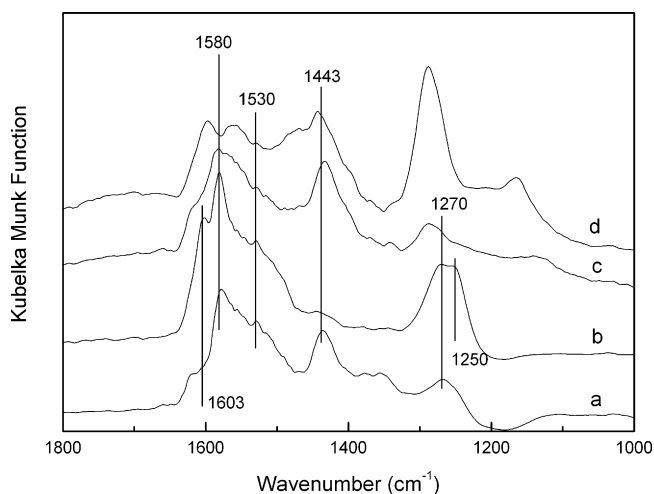


Fig. 11. In situ DRIFT spectra for Mn(0.4)/TiO₂ and Fe(0.1)–Mn(0.4)/TiO₂ exposed to 1000 ppm NO + 2% O₂ for 30 min and purged by He for 30 min ((a) and (b)), and then exposed to 1000 ppm NH₃ ((c) and (d)).

1630 cm^{−1} was stronger than on Mn(0.4)/TiO₂. We could assign 1603 and 1250 cm^{−1} to nitrates on Fe₂O₃ [24], and the bands in the range of 1600–1630 cm^{−1} could be due to NO₂ [25]. The bands at 1580, 1530 and 1270 cm^{−1} were assigned to nitrate on manganese oxides [4,22,26], which were also much stronger on Fe(0.1)–Mn(0.4)/TiO₂. When the catalysts were purged with NH₃ for 30 min (as shown in (c) and (d)), NO₂ and nitrates were gradually reduced. Thus, it was possible to conclude that NO₂ and nitrate were the active component reacting with NH₃. In this procedure, the band at 1443 cm^{−1} which was due to NH₄⁺ was formed, and it might be due to the formation of NH₄NO₃ [27]. Although the amount of nitrate was higher on Fe(0.1)–Mn(0.4)/TiO₂, it was consumed more quickly than on Mn(0.4)/TiO₂. In spectrum c, the band at 1580 cm^{−1} could still be visible, whereas in spectrum d, it had completely disappeared. It implied that the nitrate on Fe(0.1)–Mn(0.4)/TiO₂ was more active than on Mn(0.4)/TiO₂. In this

study, by using Fe(0.1)–Mn(0.4)/TiO₂, more NO was oxidized to these component, and the nitrate formed was much easier to react with NH₃. Therefore, the formation of the solid solution could improve the oxidation of NO and reduced the stability of the intermediate product, thereby giving some contributions to the increase of the catalytic activity.

3.4. Assumption model for the effect of transition metals on the catalysts

It was known from Table 1 that the nano-structure of the catalyst was improved with the addition of transition metals. And the results of XRD showed that crystallization of the catalysts was reduced. Furthermore, it could be seen in micrograph of TEM and EDS that the degree of the crystallinity progressively decreased in the centre of the particle, and manganese oxides could be well dispersed. According to XPS data, there were some other peaks appeared due to the formation of solid solution. Therefore, it could be concluded that the transition metals had interacted with manganese oxides and titania, preventing the sintering, and then higher catalytic activity was obtained.

Fig. 12 showed an assumption model for the Mn(0.4)/TiO₂ and M(0.1)–Mn(0.4)/TiO₂, which could describe the experimental results obtained with the measurements mentioned above. In the dried Mn(0.4)/TiO₂ catalyst, the amorphous manganese oxides were dispersed in TiO₂. When the catalyst was calcined, the sintering would occur. The particles would grow and agglomerate, and then crystalline MnO₂ was formed. As mentioned above, the crystalline MnO₂ has a negative effect on NO conversion. Therefore, when the ratio of Mn/Ti was more than 0.4, the sintering would lead to the formation of large amount of crystalline MnO₂, leading to the reduction of catalytic activity.

After transition metals were added, transition metal oxides were formed between the particles of manganese oxides and

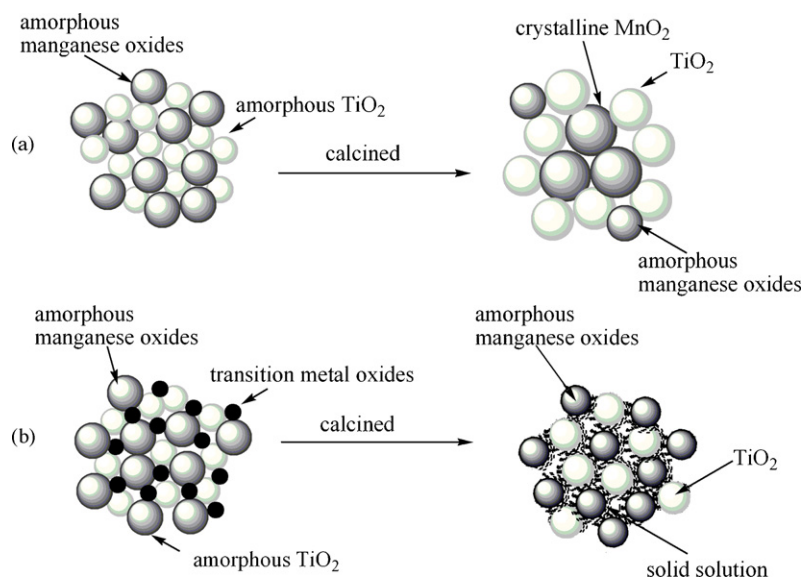


Fig. 12. An assumption model for (a) Mn(0.4)/TiO₂ and (b) M(0.1)–Mn(0.4)/TiO₂ before and after calcination.

titania. When the catalyst was calcined, the oxides would react with manganese oxides and titania, and then formed solid solutions. The particles of manganese oxides and titania in the centre of the particles would be covered with a layer of solid solution, and could not agglomerate to form crystal phase. Thus, manganese oxides could still exist as amorphous phase, and was better dispersed in these catalysts than that in Mn/TiO₂. Furthermore, NO could be oxidized more easily on the solid solution, and the groups (NO₂ and nitrates) formed on M(0.1)–Mn(0.4)/TiO₂ was more active than on Mn(0.4)/TiO₂, leading to a better reaction process. Then the catalytic activity of catalysts would increase and the negative effect of increasing manganese loading was weakened.

4. Conclusions

In this study, we investigated the Mn(*z*)/TiO₂ and the catalysts with the addition of transition metals (including Fe, Cu, Ni and Cr). The main conclusions were drawn as follows:

1. With the addition of transition metals, the activity of the catalysts increased greatly, and the negative effect of increasing the manganese oxides was weakened when the ratio of Mn/Ti increased from 0.4 to 0.6. Among these transition metals, Fe had the most favorable effect on the catalytic activity.
2. The catalysts were characterized by BET, XRD, TEM, EDS and XPS. Manganese oxides were better dispersed in the catalysts with transition metals, and these metals were found to interact with manganese oxides and titania, formed solid solution. Therefore, the better dispersion of Mn and Ti was obtained, and the surface area and pore volume was higher.
3. From the in situ DRIFT data, NO₂ and nitrate were active components in the SCR reaction. With the solid solution, NO could be more easily converted to these components, and a higher catalytic activity could be obtained.
4. An assumption model had been developed to analyze the nano-structure of the catalyst. From this model, the behavior of the transition metals was simulated. The addition of transition metals could segregate the particles of manganese oxides and titania. And the particles were prevented from sintering so that the manganese oxides were kept in amorphous phase. Therefore, the catalytic activity was significantly improved.

Acknowledgments

The project is financially supported by the National Natural Science Foundation of China (NSFC-20577040) and New Century Excellent Scholar Program of Ministry of Education of China (NCET-04-0549).

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